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TWO-PART EPOXY ADHESIVES WITH IMPROVED FLEXIBILITY AND PROCESS FOR MAKING AND USING SAME

BACKGROUND OF THE INVENTION

[0001] This application is a continuation-in-part of U.S. Application Serial No. 10/269,800, filed October 14, 2002, entitled "Two-Part Epoxy Adhesives With Improved Flexibility And Process For Making And Using Same," the disclosure of which is incorporated herein by reference.

[0002] This invention relates to two-part epoxy adhesives which have improved flexibility and a process for making and using them. More particularly, this invention relates to an improved epoxy adhesive which has good adhesion to various substrates, especially where a high level of elongation is needed due to thermal expansion and contraction of the substrates or where the substrates are exposed to thermal shock. It can also be used at low operating temperatures.

[0003] Polymeric compositions based on the commercially available Bisphenol A based epoxy resins cured by one or more of the active hydrogen compounds, such as polyamines, polyacids, polyphenols, and the like, exhibit good adhesion properties towards various substrates including metal and plastics, but most of these adhesives are rigid, stiff and brittle polymers. There is also a problem of shrinkage occurring in the epoxide adhesive during the curing, thus building undesired stress in the substrates, as well as in the adhesive at the glue line. Accordingly, it has been suggested that flexibilizers such as butadiene rubbers, urethane elastomers, and the like be added to the epoxy resins.

[0004] Past attempts to modify epoxies involved reacting them with copolymers of butadiene, acrylonitrile or other "rubber"-based compositions. See Journal of Applied Polymer Science, Vol. 26, pp. 907-919 (1981). By reacting an epoxy with those compounds and then processing the modified composition to induce in situ phase separation, "rubber rich" domains within the epoxy composition are created. Those domains improve the toughness of the cured epoxy matrix once it is formed. However, while such modified epoxy compositions are tougher and less brittle at room temperature, improvements at lower temperatures prove to be, at best,

marginal. Further, using the above-mentioned rubber-based material incurs processing problems due to an increase in viscosity of the adhesive mixture.

[0005] Accordingly, various epoxy adhesive formulations have been proposed to address these problems. See, for example U.S. Patents No. 4,728,384; 5,098,505; 5,218,063; 5,367,006 and 5,679,730. More recently, there has been introduced Mr. Sticky's Underwater Glue. According to the website at underwaterglue.com, this is an improved two-part epoxy glue having a flexibility (elongation) of 30%, very good shock dampening, and flexible bonds. It has a mixture working life of 30-60 minutes and an initial curing time of 3-4 hours. The complete curing time is 24 hours.

[0006] Still, there is a need for an even more improved two-part epoxy adhesive.

SUMMARY OF THE INVENTION

[0007] That need is met by the present invention which provides a two-part epoxy adhesive with improved flexibility and provides a process for adhering at least two substrate surfaces to each other with that adhesive.

[0008] In one embodiment, the two-part epoxy adhesive has a resin component made up of a mixture of an epoxy resin such as a standard, undiluted, liquid Bisphenol-A resin, and an internally flexibilized epoxy resin which is also preferably a Bisphenol A type resin. The resin component may also contain a plasticizer/accelerator, such as a phenol base plasticizer/accelerator, a coupling agent such as an epoxide functional silane base coupling agent, fillers, such as limestone filler and titanium dioxide white pigment, and a thixotropic agent.

[0009] The percentages by weight in the preferred embodiment of the resin component are:

30-75 % epoxy resin,
5-40% internally flexibilized epoxy resin,
5-40% plasticizer/accelerator,
0.1-1% coupling agent,
11-45% filler, and
1-8% thixotropic agent.

[0010] The two-part epoxy adhesive has a hardener component made up of a mixture of a flexibilizer, such as an amine terminated butadiene acrylonitrile adduct, and an unmodified aliphatic amine, such as an unmodified glycol ether base aliphatic amine, or a modified aliphatic amine, such as an Aminoethyl-piperazine (AEP) base modified amine, or an unmodified or modified polyamide, or combinations thereof. The hardener component may also contain an accelerator, which is preferably a tertiary amine accelerator, as well as a thixotropic agent.

[0011] The percentages by weight in the preferred embodiment of the hardener component are:

20-80% flexibilizer,
5-30% unmodified aliphatic amine,
1-10% accelerator,
10-50% modified aliphatic amine,
0-15% unmodified or modified polyamide, and
1-8% thixotropic agent.

[0012] The most preferred two-part epoxy adhesive has:

a) a resin component comprising a mixture of:
   40-45% Bisphenol A epoxy resin,
   8-15% internally flexibilized Bisphenol A type epoxy resin,
   10-20% phenol base plasticizer/accelerator,
   0.3-0.6% epoxide functional silane base coupling agent,
   15-25% limestone filler,
   0.5-2% white pigment and
   4-6% thixotropic agent, and
b) a hardener component comprising a mixture of:
   40-45% amine terminated butadiene acrylonitrile adduct,
   7-15% unmodified glycol ether base aliphatic amine,
   5-8% tertiary amine accelerator,
   25-40% AEP base modified amine, and
   1-8% thixotropic agent.

[0013] In another embodiment, the two part epoxy adhesive is free of nonylphenol and has a resin component free of nonylphenol made up of a mixture of an epoxy resin such as a standard, undiluted, liquid Bisphenol-A resin, and an internally flexibilized epoxy resin which is also preferably a Bisphenol A type resin. The resin component may also contain a plasticizer/accelerator, such as a phenol base plasticizer/accelerator free of nonylphenol, a coupling agent such as an epoxide functional silane base coupling agent, fillers, such as limestone filler and titanium dioxide white pigment, and a thixotropic agent.

[0014] The percentages by weight in the preferred embodiment of the resin component free of nonylphenol are:

30-75 % epoxy resin,

5-40% internally flexibilized epoxy resin,

5-40% plasticizer/accelerator free of nonylphenol,

0.1-1% coupling agent,

11-45% filler, and

1-8% thixotropic agent.

[0015] The two-part epoxy adhesive free of nonylphenol has a hardener component free of nonylphenol made up of a mixture of a flexibilizer, such as an amine terminated butadiene acrylonitrile adduct; an unmodified aliphatic amine, such as an unmodified glycol ether base aliphatic amine or unmodified AEP aliphatic amine, or a modified aliphatic amine, or an unmodified or modified polyamide, or combinations thereof, and a plasticizer/accelerator free of nonylphenol. The hardener component may also contain an accelerator, which is preferably a tertiary amine accelerator, as well as a thixotropic agent.

[0016] The percentages by weight in the preferred embodiment of the hardener component free of nonylphenol are:

30-80% flexibilizer,

5-45% unmodified aliphatic amine,

0-15% modified aliphatic amine,

0-15% unmodified or modified polyamide,

1-10% accelerator,

5-20% plasticizer/accelerator, and

1-8% thixotropic agent.

[0017] The most preferred two-part epoxy adhesive free of nonylphenol has:

a) a resin component free of nonylphenol comprising a mixture of:

45-55% Bisphenol A epoxy resin,

8-15% internally flexibilized Bisphenol A type epoxy resin,

10-20% dinonylphenol base plasticizer/accelerator,

0.3-0.6% epoxide functional silane base coupling agent,

15-25% limestone filler,

0.5-2% white pigment and

4-6% thixotropic agent, and

b) a hardener component free of nonylphenol comprising a mixture of:

55-65% amine terminated butadiene acrylonitrile adduct,

7-15% unmodified glycol ether base aliphatic amine,

5-8% unmodified AEP aliphatic amine,

5-8% tertiary amine accelerator,

8-15% dinonylphenol plasticizer/accelerator, and

4-6% thixotropic agent.

[0018] After the resin component and hardener component are mixed and reacted, the cured epoxy adhesive has a tensile elongation at room temperature of greater than 30%. The most preferred embodiment for the adhesive containing nonylphenol has a tensile elongation at room temperature of greater than 120%, while the most preferred embodiment for the adhesive free of nonylphenol has a tensile elongation at room temperature of greater than 80%.

[0019] In addition, the reactive mixture of resin component and hardener component has an initial cure time of less than 3 hours, and the most preferred embodiment thereof has an internal cure time of about 1.5-2 hours. The complete cure takes place in approximately 24 hours.

[0020] The epoxy adhesive of the present invention has good adhesion to various substrates including concrete, metals, plastics, and wood, and is especially useful in applications

where a high level of elongation (for example, when bonding to flexible PVC) is needed due to thermal expansion and contraction of the substrates (for example when bonding metal to plastic) or where the substrates are exposed to thermal shock. It is also useful in applications having low operating temperatures. While the preferred application temperature range is 40-100°F, it may be used at temperatures of up to about 180-200°F and down to below zero to adhere at least two substrate surfaces to each other by intercalating between those surfaces an adhesive, formed from the reactive mixture of the resin component and the hardener component disclosed above, by applying these components in equal amounts (parts by volume) from a double-barreled cartridge, mixing well until the mixture is relatively homogeneous and applied relatively evenly to the substrates, and then allowing the adhesive to cure.

DETAILED DESCRIPTION OF THE INVENTION

[0021] The present invention provides an improved two-part epoxy adhesive having a resin component and a hardener component which can be dispensed from a double-barreled cartridge in equal parts by volume concurrently and then mixed until relatively homogeneous. As is known, dispensing and mixing may be prior to application of the relatively homogeneous mixture to one or more of the substrates, or it may take place on one or more of the substrates. Likewise, a double-barreled cartridge need not be used; the resin component and hardener component can be dispensed from separate containers and then mixed. In any event, the reactive mixture of components is applied relatively evenly between substrates which are joined, and the adhesive is allowed to cure.

[0022] The initial cure takes place in less than 3 hours, and, with the two-part epoxy adhesive of the preferred embodiment, it has been found that generally the initial curing time is about 1.5 to 2.0 hours. Complete cure then takes place in about 24 hours.

[0023] After cure, the epoxy adhesive of the present invention has a tensile elongation at room temperature of greater than 30%. The most preferred embodiment for the adhesive containing nonylphenol has a tensile elongation at room temperature of greater than 120%, while the most preferred embodiment for the adhesive free of nonylphenol has a tensile elongation at room temperature of greater than 80%. Elongation is important when bonding flexible materials

like flexible polyvinyl chloride (PVC) or acrylonitrile-butadiene-styrene (ABS), and in those applications where there is a large amount of displacement between substrates, or where the degree of thermal expansion and contraction is of concern.

[0024] The improved flexibility of the two-part epoxy resin of the present invention is achieved by using a resin component and a hardener component having a unique combination of ingredients. The resin component is a mixture of epoxy resin, which may be a standard, undiluted, liquid Bisphenol A resin such as EPON 828 from Shell Oil Company, Houston, Texas, and an internally flexibilized Bisphenol A type epoxy resin such as Araldite PY 322 available from Ciba Specialty Chemicals, Tarrytown, N.Y. The internally flexibilized epoxy resins have flexible segments in their backbone. Therefore, when they react and become a part of the adhesive network, they provide flexibility into the rigid polymer via their soft/flexible segments. While Bisphenol A type resins are preferred, Bisphenol-F type resins or mixtures of the two can be used as either the core epoxy resin, or the internally flexibilized epoxy resin, or both.

[0025] The resin component may also contain a plasticizer/accelerator which may be a phenol based plasticizer/accelerator such as nonylphenol from GE Specialty Chemicals, Morgantown, W.Va. Other plasticizers/accelerators may be used. Nonylphenol is one preferred material since it has minimal effect on physical properties and is a mild accelerator.

[0026] A small amount of coupling agent is also preferably added to the resin component. Preferred is an epoxide functional silane base coupling agent such as Silane Z-6040 from Dow Corning Corporation, Midland, Michigan. That type of coupling agent, has dual reactivity, meaning that silanes, as is known, possess both organic and inorganic functionality that allow them to react with organic polymers and inorganic surfaces. An amino silane or other types of coupling agents could be used to get the same effect.

[0027] Any number of types of fillers can be added to the resin component. Preferred are limestone filler such as Marble White 325 from Filler Products Inc. and Titanium Dioxide R-900 white pigment from DuPont de Nemours, Wilmington, Delaware. Other white fillers and white pigments may be used for a white or off white colored resin component. If another color is desired, then fillers and pigments of the desired color would be used.

[0028] Finally, the resin component can contain a thixotropic agent such as Cab-o-Sil 720 from Cabot Corporation, Boston, Mass. There are numerous other thixotropic agents that could be used along with the fillers to obtain a resin component having the desired viscosity, i.e. one which permits dispensing as discussed above.

[0029] In preparation of the resin component, the core epoxy resin (EPON 828), the reactive flexibilizer (Araldite PY 322), the plasticizer/accelerator, and the coupling agent (Silane Z-6040) are mixed until the mixture is relatively homogenous, and then the fillers (Marble White 325 and Titanium Dioxide R-900) are added and mixed. As the last step, the thixotropic agent (Cab-o-Sil 720) is added and mixed until it is dispersed therein.

[0030] The preferred weight percentage range of the ingredients in the resin component and the most preferred range are as follows:

RESIN COMPONENT	Preferred	Most Preferred
Epoxy Resin	30-75	40-45
Internally Flexibilized Resin	5-40	8-15
Plasticizer/Accelerator	5-40	10-20
Coupling Agent	0.1-1	0.3-0.6
Limestone Filler	10-40	15-25
White Pigment	1-5	0.5-2
Thixotropic Agent	1-8	4-6

[0031] The hardener component contains a mixture of a flexibilizer, which may be an amine terminated butadiene acrylonitrile adduct, such as Hycor ATBN 1300X16 from B.F. Goodrich, Akron, Ohio, and an unmodified aliphatic amine, such as an unmodified glycol ether base aliphatic amine (i.e. Ancamine 1922A from Air Products, Pittsburgh, Pa.), or a modified base aliphatic amine such as an Aminoethyl-piperazine (AEP) base modified (Ancamine 1767, also from Air Products), or preferably a combination of the two. An unmodified or modified polyamide could also be used, either alone or in combination with an unmodified or modified aliphatic amine. The flexibilizer does not have to be an amine terminated butadiene acrylonitrile (ATBN) but it should be similar in nature. For example, a carboxyl terminated butadiene acrylonitrile (CTBN) can be used. Likewise, unmodified aliphatic amines other than glycol ether based ones can be used as long as they contribute to the toughness, resiliency and shock

resistance of the cured adhesive, and modified aliphatic amines other than AEP based ones can be used as long as they contribute to the toughness and speed up the cure, as do the AEP based ones.

[0032] The hardener component may also contain an accelerator, which may be a tertiary amine accelerator, such as Ancamine K-54 also from Air Products and a thixotropic agent, which can be the same as the one used in the resin component such as Cab-o-Sil 720 from Cabot. As was the case with the resin component, any thixotropic agent in an amount sufficient to give the desired viscosity may be used.

[0033] In preparation of the hardener component, all of the liquids, i.e., everything except the thixotropic agent, are blended, and then the thixotropic agent is added and mixed until well dispersed therein.

[0034] The preferred weight percentage range of the ingredients in the hardener component and the most preferred range are as follows:

HARDENER COMPONENT	Preferred %	Most Preferred %
Flexibilizer	20-80	40-45
Unmodified Aliphatic Amine	5-30	7-15
Modified Aliphatic Amine	10-50	25-40
Unmodified or Modified Polyamide	0-15	0-10
Accelerator	1-10	5-8
Thixotropic Agent	1-8	5-8

[0035] In another embodiment, the two-part epoxy adhesive is free of nonylphenol. For this embodiment, the preferred weight percentage range of the ingredients in the resin component, which is free of nonylphenol, and the most preferred range are as follows:

RESIN COMPONENT	Preferred	Most Preferred
Epoxy Resin	30-75	45-55
Internally Flexibilized Resin	5-40	8-15
Plasticizer/Accelerator Free of Nonylphenol	5-40	10-20
Coupling Agent	0.1-1	0.3-0.6
Limestone Filler	10-40	15-25
White Pigment	1-5	0.5-2

Thixotropic Agent	1-8	4-6

[0036] The preferred weight percentage range of the ingredients in the hardener component, which is free of nonylphenol, and the most preferred range are as follows:

HARDENER COMPONENT	Preferred %	Most Preferred %
Flexibilizer	30-80	55-65
Unmodified Aliphatic Amine	5-45	10-25
Modified Aliphatic Amine	0-15	0-8
Unmodified or Modified Polyamide	0-15	0-10
Accelerator	1-10	5-8
Plasticizer/Accelerator Free of Nonylphenol	5-20	8-15
Thixotropic Agent	1-8	4-6

[0037] The same epoxy resins, internally flexibilized resins, coupling agents, fillers, thixotropic agents, flexibilizers, unmodified aliphatic amines, and accelerators described above can be used in this embodiment, except that compounds containing nonylphenol should not be used. For example, the plasticizer/accelerator free of nonylphenol used in the resin and hardener components is desirably dinonylphenol, available from Huntsman, Salt Lake City, UT. Ancamine 1767, which is an AEP modified base aliphatic amine containing nonylphenol, should not be used. A modified amine which does not contain nonylphenol should be used instead. Unmodified AEP, available from Air Products, can be used as the unmodified aliphatic amine, either alone or in combination with another unmodified aliphatic amine. An unmodified or modified polyamide could also be used, either alone or in combination with an unmodified or modified aliphatic amine.

[0038] While two-part epoxy adhesives of the present invention are preferably used at 40-100°F they may be used at temperatures up to about 180-200°F, and are particularly useful at low temperatures down below about 0°F. They may be used for indoor or outdoor repair situations or in manufacturing OEM products where strong, flexible, but relatively permanent bonds are desired. They have good adhesion to various substrates including concrete, metals, such as steel, aluminum, brass, etc, plastics, such as ABS, PVC, flexible PVC, fiberglass, acrylics, polyurethanes, etc., and wood.

EXAMPLE 1

[0039] Example 1 is a formulation containing nonylphenol. The resin component and hardener component were prepared by mixing the following ingredients as described above to prepare the two-part epoxy adhesive of the present invention:

RESIN		
Tradename	**Ingredient**	**Parts by Weight**
Epon 828	Bisphenol A Epoxy Resin	49.5
Araldite PY322	Internally Flexibilized Bisphenol A Epoxy Resin	10.0
Nonylphenol	Plasticizer/Accelerator	16.5
Silene Z-6040	Coupling Agent	0.5
Marble White 325	Limestone Filler	17.0
Titanium Dioxide R-900	White Pigment	1.0
Cab-o-Sil 720	Thixotropic Agent	5.5

HARDENER		
Tradename	**Ingredient**	**Parts by Weight**
Hycar ATBN 1300x-16	Flexibilizer	41.7
Ancamine 1922A	Unmodified Aliphatic Amine	10.6
Ancamine 1767	Modified Aliphatic Amine	35.0
Ancamine K-54	Accelerator	6.7
Cab-o-Sil 720	Thixotropic Agent	6.0

[0040] The properties of the two-part epoxy adhesive containing nonylphenol were then compared to Mr. Sticky's Underwater Glue with the following results:

Properties		**Mr. Sticky's Underwater Glue (data reported)**	**Mr. Sticky's Underwater Glue (tested data)**	**Present Invention (tested data)**
Color		Off-White	Off-White	Off-White
Viscosity @ 20°C				
	Resin			35,000
	Hardener	200,000		36,000
	Mixed Viscosity			35,000
Density (gr./cc)				

	Resin	1.25		1.25
	Hardener	0.94		0.97
Mixing Ratio				
	by weight	4:3		1.2:1
	by volume	1 to 1		1 to 1
Working Life		30-60 minutes		25-30 minutes
Gell Time (25 gram)		3-4 hours		1.5-2 hours
Full Cure		24 hours		24 hours
Application Temperature		40°-100°F		40°-100°F
TYPICAL PROPERTIES OF CURED PRODUCT				
Tensile elongation		30%		125%
Tensile Modulus		76,000 psi		
Tensile Strength		2,000 psi		1,540 psi
Flexural Modulus		82,000 psi		
LAP SHEAR TESTING				
CRS/CRS @ .010"		1,800 psi	1,600 psi	1,600 psi
RIGID PVC/PVC		1,300 psi	500 psi	1,100 psi
ABRAIDED RIGID PVC/PVC		1,800 psi	850 psi	1,140 psi
ABS/ABS		400 psi	400 psi	800 psi
ABRAIDED ABS/ABS		600 psi	710 psi	875 psi
180° T–PEEL TESTING				
RIGID PVC/FLEXIBLE PVC		12.6 pli	10.4 pli	10.5 pli
ABRAIDED RIGID PVC/ FLEXIBLE PVC		25.4 pli	6 pli	10.1 pli
ABS/FLEXIBLE/PVC		13.0 pli	3 pli	10 pli
ABRAIDED ABS/FLEXIBLE/ PVC		N/A	11.1 pli	13.4 pli

EXAMPLE 2

[0041] Example 2 is a formulation free of nonylphenol. The resin component free of nonylphenol and the hardener component free of nonylphenol were prepared by mixing the following ingredients as described above to prepare the two-part epoxy adhesive free of nonylphenol of the present invention:

RESIN		
Tradename	**Ingredient**	**Parts by Weight**
Epon 828	Bisphenol A Epoxy Resin	50
Araldite PY322	Internally Flexibilized Bisphenol A Epoxy Resin	10
Dinonylphenol	Plasticizer/Accelerator Free of Nonylphenol	16
Silene Z-6040	Coupling Agent	0.5
Marble White 325	Limestone Filler	17
Titanium Dioxide R-900	White Pigment	1
Cab-o-Sil 720	Thixotropic Agent	5.5

HARDENER		
Tradename	**Ingredient**	**Parts by Weight**
Hycar ATBN 1300x-16	Flexibilizer	60
Ancamine 1922A	Unmodified Aliphatic Amine	10
AEP	Unmodified Aliphatic Amine	6
Ancamine K-54	Accelerator	7
Dinonylphenol	Plasticizer/Accelerator	11
Cab-o-Sil 720	Thixotropic Agent	6

[0042] The properties of the two-part epoxy adhesive free of nonylphenol were then compared to Mr. Sticky's Underwater Glue with the following results:

Properties	**Mr. Sticky's Underwater Glue (data reported)**	**Mr. Sticky's Underwater Glue (tested data)**	**Present Invention (tested data)**
Color	Off-White	Off-White	Off-White
Working Life	30-60 minutes		25-30 minutes
Gell Time (25 gram)	3-4 hours		1.5-2 hours
Full Cure	24 hours		24 hours
Application Temperature	40°-100°F		40°-100°F
TYPICAL PROPERTIES OF CURED PRODUCT			
Tensile elongation	30%		80%
Tensile Modulus	76,000 psi		
Tensile Strength	2,000 psi		1,300 psi
Flexural Modulus	82,000 psi		

LAP SHEAR TESTING			
CRS/CRS @ .010"	1,800 psi	1,600 psi	1,900 psi
RIGID PVC/PVC	1,300 psi	500 psi	800 psi
ABRAIDED RIGID PVC/PVC	1,800 psi	850 psi	
ABS/ABS	400 psi	400 psi	600 psi
ABRAIDED ABS/ABS	600 psi	710 psi	
180° T-PEEL TESTING			
RIGID PVC/FLEXIBLE PVC	12.6 pli	10.4 pli	10.5 pli
ABRAIDED RIGID PVC/ FLEXIBLE PVC	25.4 pli	6 pli	10.5 pli
ABS/FLEXIBLE/PVC	13.0 pli	3 pli	8.7 pli
ABRAIDED ABS/FLEXIBLE/ PVC	N/A	11.1 pli	12.4 pli

[0043] While certain representative embodiments and details have been shown for purposes of illustrating the invention, it will be apparent to those skilled in the art that various changes in the compositions and methods disclosed herein may be made without departing from the scope of the invention, which is defined in the appended claims.

What is claimed is: